

# Preliminary study of KNN thin films doped by rare-earths for sensor applications

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**ABSTRACT** – Among ferroelectrics systems, potassium sodium niobate (KNN) has drawn much attention due to a clear-cut advantage of high piezoelectric and ferroelectric performances. The volatility of alkaline element (K,Na) is detrimental to the stoichiometry of KNN, contributing to the formation of intrinsic defects. Thus, the primary goal of this study is to design a solution to overcome the volatility issue of KNN. Introduction of rare-earth cations in the host KNN could reduce the vacancies in KNN. Currently, three arrays of dopants were integrated into KNN. In this preliminary work, a sol-gel technique was employed to produce a thin film that can be utilized later in the sensor applications. The structural and electrical properties were characterized using Raman spectroscopy and 2-point probe equipment, respectively. The typical Raman spectra of KNN thin films were shifted towards lower or higher wavenumbers depending on the cations deficiencies or redundancies. The conductivity of thin films was found to be increased as the dopant concentration was increased.

## 1. INTRODUCTION

Alkaline niobate, in particular, potassium sodium niobate, ( $K_xNa_{1-x}$ )  $NbO_3$  (KNN) is derived from a combination of simple perovskite structure of  $KNbO_3$  (KN) and  $NaNbO_3$  (NN). It has a high Curie temperature (420°C) and exhibits good ferroelectric and piezoelectric properties. However, the proportion of K, Na, and Nb is likely to deviate from stoichiometry due to the evaporation of K and Na at high temperature. Theoretically, the formation of intrinsic defects in the perovskite structure results in reduced ferroelectric and piezoelectric properties [1].

Substitutions of several cations in KNN structure would improve the properties of KNN-based ceramics. Improvement of properties is believed due to the coexistence of orthorhombic-tetragonal phases at room temperature. This occurrence allows a better electrical poling process because of the existence of more crystallographic directions for the polarization [2-4]. Rare-earth elements (i.e. Ce, La, Nd) are dominant dopants to be substituted for KNN-based materials. It was stated that rare-earth elements are known to demonstrate useful functions of stabilizing and lowering dissipation factor in dielectric ceramics [5]. In previous

work on lead-free barium titanate (BT), it was found that the appropriate amount of rare-earth in KNN could enhance the electrical properties of BT [3]. A similar idea could be addressed to compensate the volatility of K and Na in KNN. For this reason, the present study is concentrated on the doping elements in KNN materials in response to having excellent properties. Different content of dopants were used in this study.

## 2. METHODOLOGY

There are several stages to fabricate rare-earths doped KNN. Two alkali precursors that are potassium acetate and sodium acetate were used as starting solutions. The precursors were mixed with rare-earth nitrate-based, i.e., and yttrium nitrate hexahydrate. Different content of rare-earth were used in this work ( $Y = 0, 0.25, 0.5$ ). These chemicals were dissolved in a polar organic solvent, 2-methoxyethanol with constant stirring at room temperature. Then, niobium ethoxide was added to the mixture solution. To retain the stability of the niobium ethoxide, acetylacetone was introduced to the prepared solution.

The solution was then deposited on the Si substrate to produce the thin films. The films were spun onto the wafer at 2000-3000 rpm for 60 seconds. After spinning, the wet films were heated at 200°C for 5 minutes. Then, the thin films were annealed for 30 minutes at 650°C in the furnace.

Subsequently, Raman microprobe measurements were used to study the changes in the Raman scattering modes of KNN thin films prepared with different yttrium contents. Later, the electrical properties were observed using I-V measurement by 2-point probe equipment.

## 3. EXPECTED RESULTS AND DISCUSSION

Raman spectra of KNN thin films with different yttrium content are depicted in Figure 1. The Raman-active mode  $\nu_1$ ,  $\nu_2$  and  $\nu_3$  correspond to the stretching modes of  $NbO_6$  octahedra [6]. The peak position shifted toward the higher wavenumber side (619 to 621  $cm^{-1}$ ) as the yttrium (Y) concentration increase up to 0.5%. According to Hardcastle and co-worker, the peak shifting to a higher wavenumber was due to an increase in the binding strength [7]. This change was attributed to the shortening distance between  $Nb^{5+}$  and a

coordinate of the oxygen atom. Additionally, the peak shift occurs when the A-site in the  $ABO_3$  crystal structure was integrated with a smaller ion.

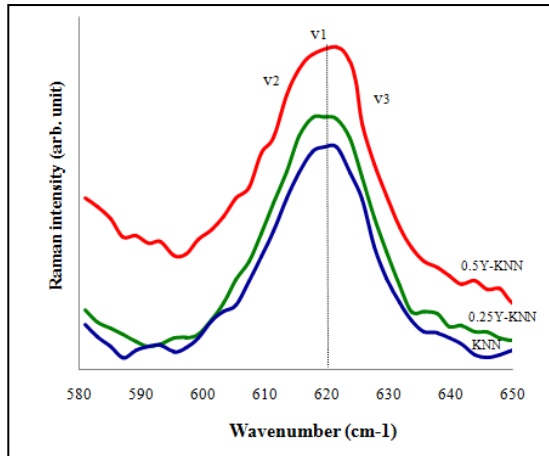


Figure 1 Magnified Raman spectra with vibration changes of stretching mode  $v_1$ .

The I-V characteristics of the KNN thin films recorded at room temperature are shown in Figure 2. Current increase as more yttrium dopant was introduced in KNN thin films. From the graph, it presented that the most conductive sample is 0.5% Y-KNN and the least conductive is undoped KNN. The increase in conductivity is due to more free electrons were generated by integrating Y ions which increase the carrier concentration in thin film [8].

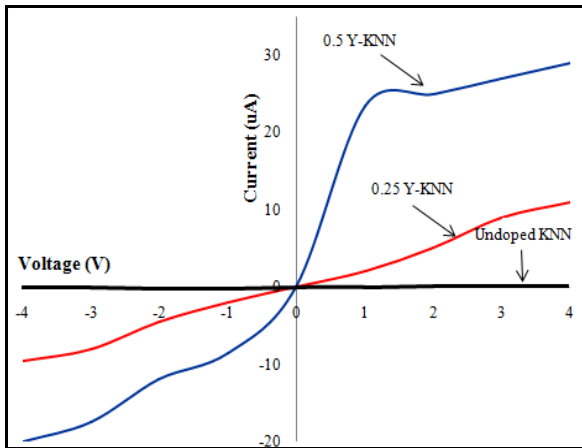


Figure 2 I-V characteristics of KNN thin films at various dopant concentration

#### 4. CONCLUSIONS

The KNN thin films were successfully fabricated by sol-gel method. Raman spectra indicate that the variation of peak shifting around  $619\text{ cm}^{-1}$  attributed to the enhancement of binding strength dominated by dopant concentration. Meanwhile, the I-V measurements show that the thin film conductivity was high at 0.5% Y-doped KNN. Hence, the encouraging results could contribute to the incorporation of these thin films in sensor devices.

#### 5. ACKNOWLEDGMENT

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